



# Surface modification of cotton fabrics by gas plasmas for color strength and adhesion by inkjet ink printing



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## ABSTRACT

Surface properties of cotton fabric were modified by three types of gas plasma pretreatment, namely, oxygen (O<sub>2</sub>), nitrogen (N<sub>2</sub>) and sulfur hexafluoride (SF<sub>6</sub>), to improve ink absorption of water-based pigmented inkjet inks and color reproduction of the treated surfaces. Effects of gas plasma exposure parameters of power, exposure time and gas pressure on surface physical and chemical properties of the treated fabrics were investigated. XPS (X-ray photoelectron spectroscopy) was used to identify changes in functional groups on the fabric surface while AFM (atomic force microscopy) and SEM (scanning electron microscopy) were used to reveal surface topography of the fabric. Color spectroscopic technique was used to investigate changes in color strength caused by different absorptions of the printed fabrics. The O<sub>2</sub> plasma treatments produced new functional groups, —O—C—O/C=O and O=C=O while N<sub>2</sub> plasma treatments produced additionally new functional groups, C—N and O=C—NH, onto the fabric surface which increased hydrophilic properties and surface energy of the fabric. For cotton fabric treated with SF<sub>6</sub> plasma, the fluorine functionalization was additionally found on the surface. Color strength values (*K/S*) increased when compared with those of the untreated fabrics. SF<sub>6</sub> plasma-treated fabrics were hydrophobic and caused less ink absorption. Fabric surface roughness caused by plasma etching increased fabric surface areas, captured more ink, and enhanced a larger ink color gamut and ink adhesion. Cotton fabrics exhibited higher ink adhesion and wider color gamut after the O<sub>2</sub> plasma treatment comparing with those after N<sub>2</sub> plasma treatment.

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## 1. Introduction

Ink-jet printing technique is a well-known and rapidly growing process with favorable acceptance for today's textile printing. The advantages of ink-jet printing are excellent printed pattern quality, considerably little pollution and especially fast response of cloth fashion [1]. Basically, the sharpness and color appearance of the ink-jet printed images are an eye-catching selling point of

the final product. Hence, treatment of the fabric as a prerequisite must be done before printing to improve the printing qualities especially ink absorption. Traditional preprocessing is a sizing process with thickeners. This process is tedious and takes very long time with complication. In addition, some possibly toxic substances and waste water may be produced inline during processing. Among various environmentally friendly processes available, plasma technique is a popular method which has been widely used to modify the surface properties. Plasma treatment only modifies the outermost thin layer of the surface, while the bulk properties mostly remain unaffected and does not generate waste water [2,3]. The treatment produces new functional groups on the surface. Like many gas pretreatments, plasma has an aging effect. Surface roughness is another parameter which can be correlated with the amount of coating adhered to the treated surface and can be altered by the plasma treatment [4]. At present, uses of plasma to modify surfaces

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of textile fabrics have replaced most of the conventional textile pre-processing for improving dyeing properties and textile functional finishing. Fang and Zhang [5] studied the effects of exposure time, pressure and power on the polyester fabrics printed by the pigmented jet inks. The irradiation power, within 50–90 W, increased the  $K/S$  values of the printed fabric whereas the pressure and exposure time imposed maximum  $K/S$  values for each individual condition. Anti-bleeding of color of the treated fabrics was better than those without plasma treatment [5]. Fang et al. [2] used the oxygen plasma to modify surface of silk fabrics for inkjet printing in terms of color adhesion. They further studied changes of physical and chemical morphologies on fabric surface which related to better color performance. Hodak et al. [6] enhanced hydrophobicity of silk by  $SF_6$  plasma pretreatment. Apart from PET and silk fabrics, Yuen and Kan [7], Temmerman and Lcys [8], Pandiyaraj and Selvarajan [9] modified cotton fabrics by plasma treatments to achieve their particular purposes either to increase hydrophilicity or hydrophobicity.

Our previous work [10] showed that the oxygen plasma treatments improved the hydrophilicity of PET fabric. The oxygen plasma also provided fabric surface roughness and increased polar groups on the polyester surface. Contact angles of the treated fabric decreased to zero degree, a spreading phenomenon, after being treated with oxygen plasma which indicated a prospect to enhance the hydrophilicity of fabrics [10]. Pransilp et al. [11] further investigated the influences of plasma with different plasma gases namely oxygen, nitrogen, argon and sulfur hexafluoride plasma under various operating conditions on the color yield of PET fabric. The results exhibited that plasma treatment increased the degree of roughness on the fabric surface. Moreover, an incorporation of the mentioned elements from the gas plasma pretreatment in the treated fabric was found on the fabric surface by XPS (X-ray photoelectron spectroscopy). All the plasma modified PET fabric surfaces enhanced the color yield. Increases in surface roughness resulting from the plasma treatment contribute to the higher color yield. In the present research, we shall carry out an in-depth study of the influences of oxygen, nitrogen and  $SF_6$  gas plasma on color reproduction and color adhesion of the treated cotton fabric surface printed with a set of commercially available water-based pigmented inkjet ink. Changes on topography and  $K/S$  of the printed test chart upon plasma irradiation are also discussed.

## 2. Materials and methods

### 2.1. Materials

Fabric sample in this study is 100% cotton woven fabric without any brightener. The fabric has a surface density of  $88.76 \text{ g m}^{-2}$ . The density of warp and weft was  $48 \text{ ends cm}^{-1}$  and  $48 \text{ picks cm}^{-1}$ , respectively. It was used as received, without washing or treatment before plasma treatment. The fabric samples were cut to the size of A5 ( $14.8 \text{ cm} \times 21 \text{ cm}$ ). During the plasma treatment, the fabric samples were held stretched in a horizontal plane with the aid of quadrilateral frame.

### 2.2. Treatment method

#### 2.2.1. Plasma treatment

The radio-frequency inductively coupled plasma (RF-ICP) generator has been utilized to treat cotton fabric samples. The schematic diagram of RF-ICP is shown in Supplement Fig. 1. The main components of the system are the reactor chamber, the RF generator, the impedance matching network and the gas supply system. A base pressure of  $3 \times 10^{-5}$  Torr was achieved using a turbo molecular pump backed by a rotary vane pump. After the base pressure

was reached, the desired gas was fed into the chamber via mass flow controllers. The gases used in all experiments are of 99.99% purity. The fabric samples were held stretched in a horizontal plane with the aid of a holding quadrilateral frame. The samples were exposed to the plasma at the operating pressure of 0.5 Torr. The operating RF powers were varied from 50–150 W. The treatment times were set in the range of 0.5–20 min. All the characterized properties mentioned below were carried out within one day right after the plasma treatment.

Supplementary Fig. 1 related to this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apsusc.2015.12.102>.

#### 2.2.2. Ink-jet printing procedure

After the plasma treatment process, the fabrics were printed with a set of four-color, pigmented ink-jet inks (cyan, magenta, yellow and black), using a commercially available water-based inkjet ink set from International Connected Trade Co., Ltd. (Thailand). The cotton fabrics were printed by the EPSON Stylus T13 printer (Seiko Epson Corporation, Japan). The Epson DURABrite Ultra pigment ink used in its printer was adopted to print on porous fabric surface instead of inkjet printing paper. Epson DURABrite Ultra pigment ink is composed of black or colored particles that are water-insoluble and are coated or encapsulated by a special resin to help them adhere to the media better and to achieve many special properties. Therefore, these particles are able to “rest” on the surface of even porous materials like plain paper, making prints look sharp and detailed, with rich black text or colors and without ink bleeds. With ink droplets of the same size, the water-based pigmented inks have a smaller spread into the fibers of a plain paper compared to dye-based inks, resulting in sharper looking text and images. The ink properties were characterized for viscosity, zeta potential, particle size and surface tension which shall be discussed in the later part of this work [12,13]. A color test chart, Gretag–Macbeth test chart, composing 294 color patches and control elements as given in Supplement Fig. 2 was used for investigating the color quality of the printed fabrics contributed by the gas plasma treatment.

Supplementary Fig. 2 related to this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apsusc.2015.12.102>.

The pigmented inkjet ink properties, as shown later in Table 1, were characterized as follows. The inks were diluted in deionized water before measuring the zeta-potential using a Nano-ZS, Zeta potential Analyzer (Malvern Instruments Ltd., UK) in a disposable U-shaped cell in which each wall can accommodate one small piece of a Cu electrode [12] to connect the measurement. Brookfield viscometer (DV III, programmable rheometer, USA) was used to measure viscosity of the inks at  $25^\circ\text{C}$ . Laser particle size distribution analyzer (Malvern laser scattering analyzer model Mastersizer S long bed Ver. 2.11, UK) was used for analyses of the particle size distribution of the pigment inks. The surface tension of the inks was measured by surface tensiometer (K8, Kruss, Germany) using the DuNouy Ring method. The measurement was performed at room temperature [13]. The mentioned property for each independent pigmented color ink was measured in triplicates.

### 2.3. Testing procedures

#### 2.3.1. Contact angle and surface energy

To investigate the wettability properties of the treated surface, contact angles and the surface energy of cotton fabric were measured. Contact angles of the surfaces were evaluated by a standard goniometry (200-F1, Rame-Hart, USA). Distilled water was dropped on the fabric surface using a micro-syringe ( $3 \mu\text{L}$ ), and the contact angles were recorded at a specific time for every measurement. Similar procedure was carried out using  $\text{CH}_2\text{I}_2$ . Then the surface

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